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(54) HAIR AND SKIN TREATMENT MEDIUM

(71) We, WELLA AKTIENGESELLSCHAFT, a German Company, of 61 Darmstadt, Berliner Allee 65, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to hair and skin treatment media containing water-soluble cerium-IV salts or their less water-soluble products obtained by reaction with higher molecular weight anion active, cation active or amphoteric substances.

Where a lasting change in the form of the hair is concerned and in fact in the case of both permanent waving and straightening the hair is conventionally treated with a reducing agent based on mercapto compounds or sulphites.

The derivatives of thioglycolic acid in particular, such as ammonium thioglycolate and glycerin monothioglycolate, are the mercapto-compounds which have been used, while of the sulphites mainly ammonium sulphite has been used. The reduction treatment of hair results in a cleavage of the disulphide bridges in the hair keratin, causing the hair to be softened so that it can easily be given the desired shape. In order to establish the hair in this new style, it is necessary to recrosslink the previously split disulphite bridges. This treatment, described as "fixing" is usually carried out with an oxidising medium, generally hydrogen peroxide. Normally this is followed by a thorough rinsing of the hair with water.

However, where such hair treatment are concerned, residues of the reducing agent or of the oxidising agent are often left in the hair. The cause often lies in an inaccurate application of these two agents and also of the rinsing agent, with regard to the quantities used and also the time required for them to act. Thus, on the one hand, by reason of inadequate fixing, residues of the reducing agent may remain in the hair while on the other hand residues of the oxidising agent can be attributed to inadequate rinsing. Certainly, however, even with very thorough rinsing, all traces of these agents

cannot be completely eliminated from the hair. This is due to the property which the hair has of binding such agents tightly to it.

The fact that such residues remain in the hair has a very disadvantageous effect on the structure and appearance of the hair since it can lead to not inconsiderable hair damage. Such damage becomes noticeable in that the hair becomes brittle and its strength diminishes; furthermore, the combing properties of the hair suffer and there is a loss of natural hair gloss. In addition, residues of reducing agents adversely affect the durability of the permanent wave while residues of the oxidising agents undesirably brighten the hair colour.

Where hair is permanently shaped with mercapto compounds which are used nowadays predominantly, however, unpleasant smells can be discerned on the hair following treatment and it is only with difficulty that they can be disguised with perfumes. The hair generally, not only the permanently waved hair, has the property of binding odours to it. This is noticeable to a very troublesome degree for the wearer in the case of unpleasant smells like those which are caused by mercapto compounds or also in the case of powerful kitchen smells.

As is well known, in the local zone of its development, the hair still has a relatively small number of disulphide bridges in the hair keratin. Up to shortly above the surface of the skin, however, this number increases constantly, so that finally a sufficient number of disulphide bonds ensures the strength of the hair. In the narrower zone, close to the scalp, where by reason of the still too small number of disulphide bridges, this strength is not present, the hair breaks easily and so falls out. These disadvantageous consequences are considerably amplified by mechanical loading of the hair constituted for example by combing and various types of hair treatment, particularly blondering. In this zone of minimal strength, the hair is also particularly capable of absorbing hair dyes which, compared with the rest of its length, results in an intensive

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- absorption of colour and thus to the formation of so-called "colour bars".
 It has been found that the disadvantage described at the outset can be avoided by using the media according to the present invention.
 These media are suitable for removing from the hair residues of reducing agents and oxidising agents such as hydrogen peroxide. In addition, they also have the capacity to firm the hair in its structure and cleanse it of intense odours. These properties make the media according to the invention particularly suitable for use as secondary treatment media following the permanent waving of the hair or as fixing agents in permanent waving or permanent straightening of crinkly hair. They can however also be used for other purposes of hair treatment, for example as hair dressing or hair treatment setting media. In particular, by reason of their capacity to firm the structure of the hair, it is also possible to use them as pre-treatment media before hair is dyed and blondered.
 Furthermore, it has been found that the media according to the present application are moreover suitable for treating the skin and of both the scalp and other parts of the body.
 This is particularly attributable to their disinfectant and deodorant properties. For example, such media can be used to fight dandruff, as deodorants, antiperspirants or special skin creams.
 According to the invention we provide a medium for hair and/or skin treatment, containing in an acid carrier a water soluble cerium-IV salt or a reaction product of a water-soluble cerium-IV salt with a higher molecular weight anion active, cation active or amphoteric substance.
 By "higher molecular weight" we mean a molecular weight of 250 to 600.
 Of the water soluble cerium-IV salts, ammonia cerium-IV nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and ammonium cerium-IV sulphate $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ are particularly useful.
 Suitable higher molecular anion active substances may for example be selected from the sulphated oils, alkyl sulphates, alkyl ether sulphates, alkyl aryl ether sulphates, alkyl sulphonates, alkyl aryl sulphonates, alkyl naphthaline sulphonates, fatty acid condensation products, sulphosuccinic acid esters, salts of alkyl polyglycol carbonic acids and alkyl benzimidazol sulphonates.
 Special representatives of these classes are racinol sulphuric acid sodium, sodium acetyl stearyl sulphate, sodium lauryl alcohol diglycol ether sulphate, ammonium isononyl phenol tetraglycol sulphate, sodium pentadecyl sulphonate, sodium lauryl benzol sulphonate, sodium dibutyl naphthaline sulphonate, sodium sulphostearic acid ethyl ester, potassium salt of stearyl amine albumin condensate, sodium salt of lauryl acid amide diglycol sulphosuccinic acid semi-ester, sodium salt of lauryl alcohol pentaoyethyl carbonic semi-ester and sodium heptadecyl benzimidazol sulphonate.
 Of the higher molecular cation active substances, particularly the classes of the quaternary ammonium salts and pyridinium compounds should be mentioned.
 Of these classes, dihexadecyl dimethyl ammonium chloride, hexadecyl trimethyl ammonium chloride, myristyl dimethyl benzyl ammonium chloride, dimethyl cetyl benzyl ammonium chloride and N-dodecyl pyridinium chloride should be mentioned.
 Preferably the classes of carboxy betains and imidazolium betains should be included among the higher molecular amphoteric substances.
 Of these classes, for example myristyl acid amide propyl dimethyl amino acetic acid betain and 1 - hydroxy - ethyl - 2 - lauryl - 4,5 - dihydro- imidazolium - 1 - carboxy methylene betain may be considered.
 Difficultly water-soluble products of reaction which may be used according to the invention should in the main include the products of reaction of on the one hand water soluble ammonium cerium-IV nitrate with higher molecular anion active or amphoteric substances and on the other water soluble ammonium cerium-IV sulphate with higher molecular cation active or amphoteric substances.
 These products of reaction are manufactured in that solutions of the water soluble cerium-IV salts and of the higher molecular surface active substances which are intended to contain the two dissolved reagents in a preferably equivalent quantitative proportion, should be stirred together. The not readily soluble products of reaction which form can be separated by centrifugal treatment and can be stirred into the corresponding carrier, for example an emulsion, while still in a somewhat moist state.
 The media according to the invention are intended to have an acid pH value, preferably pH 1.5 to 6. The concentration of the water soluble cerium-IV salts as well as their products of reaction with the previously-mentioned higher molecular surface active substances is most expediently in the range from 0.5 to 11.5% by weight.
 The water soluble cerium-IV salts have a tendency at higher pH values of the acid pH range to form difficultly soluble basic salts. Their action in the media according to the invention is however not adversely affected thereby; only a somewhat retarded action occurs. This may be of advantage in preparations where particular store is set by such a retarded release of action.
 Possible forms in which the media claimed may be prepared are for example solutions, emulsions, gels, creams, powders or aerosols corresponding to the cosmetically usual carrier

	compositions. If expedient, the micro-encapsulated form may also be used.	The shampoo has a pH value of 2.0. The hair is then rinsed with water, set in the usual way and dried.	60
5	The media may also contain cosmetically usual and known additives such as for example perfume oils, dyestuffs, buffers, revivers, clouding agents, thickeners, vitamins, plant extracts, lecithin, proteins and others.		
10	The following examples are intended to explain in greater detail the object of the patent application.	Example 4 Rinsing medium for use following permanent waving Rinse the permanently waved hair in areas using 500 ml of water in which, shortly before use, a mixture of	65
	Examples	3.0 g ammonium cerium-IV nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	
	Example 1 Rinsing medium following permanent waving The permanently waved hair is rinsed with 300 g of the following solution:	1.0 g anhydrous sodium tetraborate	70
15	1.0 g ammonium cerium-IV nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	has been dissolved. The solution has a pH value of 1.6. To finish, the hair is set in the usual way and dried.	
20	0.4 g octyl phenol oxyethylated with 20 mol ethylene oxide		
25	0.3 g perfume oil	Example 5 Hair dressing cream	75
	0.3 g ammonia, 25%	A) 1.0 g ammonium cerium-IV nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ is dissolved in 10 ml water to which 50 ml of an aqueous solution of 5.0 g sodium cetyl stearyl sulphate are added. The resultant precipitate is centrifuged off.	80
	98.0 g water	B) 8.0 g glycerin monostearate, 20.0 g paraffin oil and 2.0 g olive oil are emulsified hot with 50 g water.	
	100.0 g	The precipitate separated by centrifugal treatment from A) is then stirred into the emulsion of B), 0.3 g perfume oil are added and topped up to 100 g with water. The resultant hair dressing cream has a pH value of 6.	85
30	The solution has a pH value of 2.0. After about 3 minutes, the hair is rinsed with water, set in the usual way and dried.		
	Example 2 Cream for secondary treatment of straightened hair	Example 6 Hair treatment medium	90
35	Upon the conclusion of a hair straightening process, 30 g of the following cream are spread evenly onto the hair:	A) 1.0 g ammonium cerium-IV sulphate $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_6 \cdot 2\text{H}_2\text{O}$ is dissolved in 10 ml water and added to 25 ml of an aqueous solution of 2.5 g dimethyl lauryl benzyl ammonium chloride. The resultant precipitate is separated by centrifuge.	
40	11.5 g ammonium cerium-IV sulphate $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_6 \cdot 2\text{H}_2\text{O}$	B) 1.8 g cetyl stearyl alcohol, 0.9 g spermaceti, 1.8 g glycerin monostearate and 0.2 g of a 50% aqueous solution of dimethyl lauryl benzyl ammonium chloride are emulsified hot with 50 g water.	95
45	2.3 g cetyl stearyl alcohol	The precipitate separated by centrifuge from A) is then stirred into the emulsion of B), 0.2 g perfume oil are added and the mixture topped up to 100 g with water. The cream hair treatment medium obtained has a pH value of 5.	100
	0.3 g sodium lauryl sulphate	The cream is applied to the hair and then, to avoid drying out, covered with a synthetic plastic film hood. It is then left to act for 5 minutes under the dryer (temperature at the head approximately 45 to 50°C). In conclusion, the hair is rinsed with water, set in the usual way and dried.	105
50	0.6 g perfume oil		110
55	4.3 g ammonia, 25%		115
	37.2 g water		
	100.0 g		

Example 7**Hair setting medium**

The hair which has been permanently waved shortly before it is moistened in the usual way with a solution of the following composition:

3.0 g	polyvinyl pyrrolidone	2.0 g	ammonium cerium-IV sulphate
0.5 g	ammonium cerium-IV nitrate	(NH ₄) ₂ Ce(NO ₃) ₆	(NH ₄) ₂ Ce(SO ₄) ₂ · 2H ₂ O
0.3 g	ammonia, 25% (to adjust the pH to 2.0)	1.3 g	ammonium acetate
96.2 g	water	3.0 g	aqueous solution of sodium lauryl alcohol diglycol ether sulphate, 28%
100.0 g		93.7 g	water

10 after which the hair is wound on curlers, dried, removed from the curlers and combed into a style.

Example 8
Anti-perspirant and deodorant

0.7 g	ammonium cerium-IV nitrate	20	(NH ₄) ₂ Ce(NO ₃) ₆
0.3 g	castor oil oxyethylated with 40 mol ethylene oxide		
0.2 g	perfume oil		
0.2 g	ammonia, 25%		
98.6 g	water		
100.0 g			

This solution has a pH value of 2.0 and is sprayed onto the skin with a hand atomiser.

Example 9**Special skin cream**

A)	15.0 g	stearyl alcohol	30
	3.0 g	stearyl alcohol oxyethylated with 10 mol ethylene oxide	
	5.0 g	avocado oil	
	2.0 g	glycerin	
	40.0 g	water	
B)	1.0 g	ammonium cerium-IV nitrate	
	(NH ₄) ₂ Ce(NO ₃) ₆		
	34.0 g	water	

40 The components mentioned under A) are emulsified hot. The solution B) is then stirred into the cooled cream. The resultant skin cream has a pH value of 1.7.

Example 10**Fixing agent for permanent waving**

After the hair has been treated with a conventional thioglycolate containing waving agent, the hair, wound on curlers, is first rinsed with water, after which it is rinsed with 500 ml of a 0.5% acetic acid solution. The hair is then fixed with a solution of pH 3.5, and of the following composition:

2.0 g	ammonium cerium-IV sulphate
(NH ₄) ₂ Ce(SO ₄) ₂ · 2H ₂ O	
1.3 g	ammonium acetate
3.0 g	aqueous solution of sodium lauryl alcohol diglycol ether sulphate, 28%

55 93.7 g water

100.0 g

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Wound on curlers, the hair is foamed with half this solution, using a sponge. After it has been left for 5 minutes to act, the hair is removed from the curlers and foamed with the other half of the solution. After a further 5 minutes, the hair is rinsed out with water, set into a style in the usual way and dried.

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Example 11
Fixing agent for the straightening of crinkly hair

After the hair has first been treated with a conventional thioglycolate containing straightening agent, it is rinsed with water and treated with 500 ml water containing 5 g ammonium cerium-IV sulphate (NH₄)₂Ce(SO₄)₂ · 2H₂O in solution, as follows: the hair is first rinsed with half of this solution (pH 1.8), left for 5 minutes and then the other half is poured onto the hair. After being left for a further 3 minutes, the hair is rinsed with water and dried.

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The media according to Examples 1 to 7 are outstandingly suitable for removing from the hair both residues of reduction agents and also residues of hydrogen peroxide. At the same time, the hair is fixed in its structure, damaged hair retaining its natural consistency and its shiny appearance. Furthermore, premature breakage of hair close to the scalp is avoided and any subsequent dyeing of the hair is compensated. Since the media have moreover a disinfectant action, they have a favourable anti-dandruff action. They are furthermore suitable for cleansing the hair of unpleasant odours. The media according to Examples 5 and 7, when left in the hair, at the same time prevent the absorption of such odours.

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90 The media described in Examples 8 and 9 have an excellent deodourising and anti-perspirant action.

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95 The media according to Examples 10 and 11 produce an advantageous stabilising of the hair style and strengthen the hair structure.

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WHAT WE CLAIM IS:—

1. A medium for hair and/or skin treatment, containing in an acid carrier a water soluble cerium-IV salt or a reaction product of a water soluble cerium-IV salt with an anion active, cation active or amphoteric substance having a molecular weight from 250 to 600.

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110 2. A medium according to Claim 1 contain-

ing as the water soluble cerium-IV salt ammonium cerium-IV nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ or ammonium cerium-IV sulphate $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$.

5 3. A medium according to Claim 1 or Claim 2, containing the reaction product of ammonium cerium-IV nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ with an anion active or amphoteric substance having a molecular weight from 250 to 600.

10 4. A medium according to Claim 1 or Claim 2, containing the product of a reaction between ammonium cerium-IV sulphate $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ with a cation active or

amphoteric substance having a molecular weight from 250 to 600.

15 5. A medium according to any preceding claim and having a pH from 1.5 to 6.0.

6. A medium for hair and/or skin treatments substantially as herein described with reference to the Examples.

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